John E. McMurry • Robert C. Fay

General Chemistry: Atoms First

Chapter 4
Ionic Bonds and Some Main-Group Chemistry

Lecture Notes

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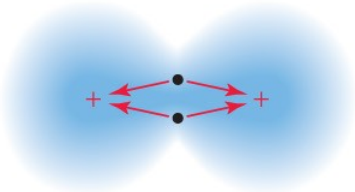
Molecules, Ions, and Chemical Bonds

Covalent Bond: A bond that results from the sharing of electrons between atoms.

The two teams are joined together because both are tugging on the same rope.

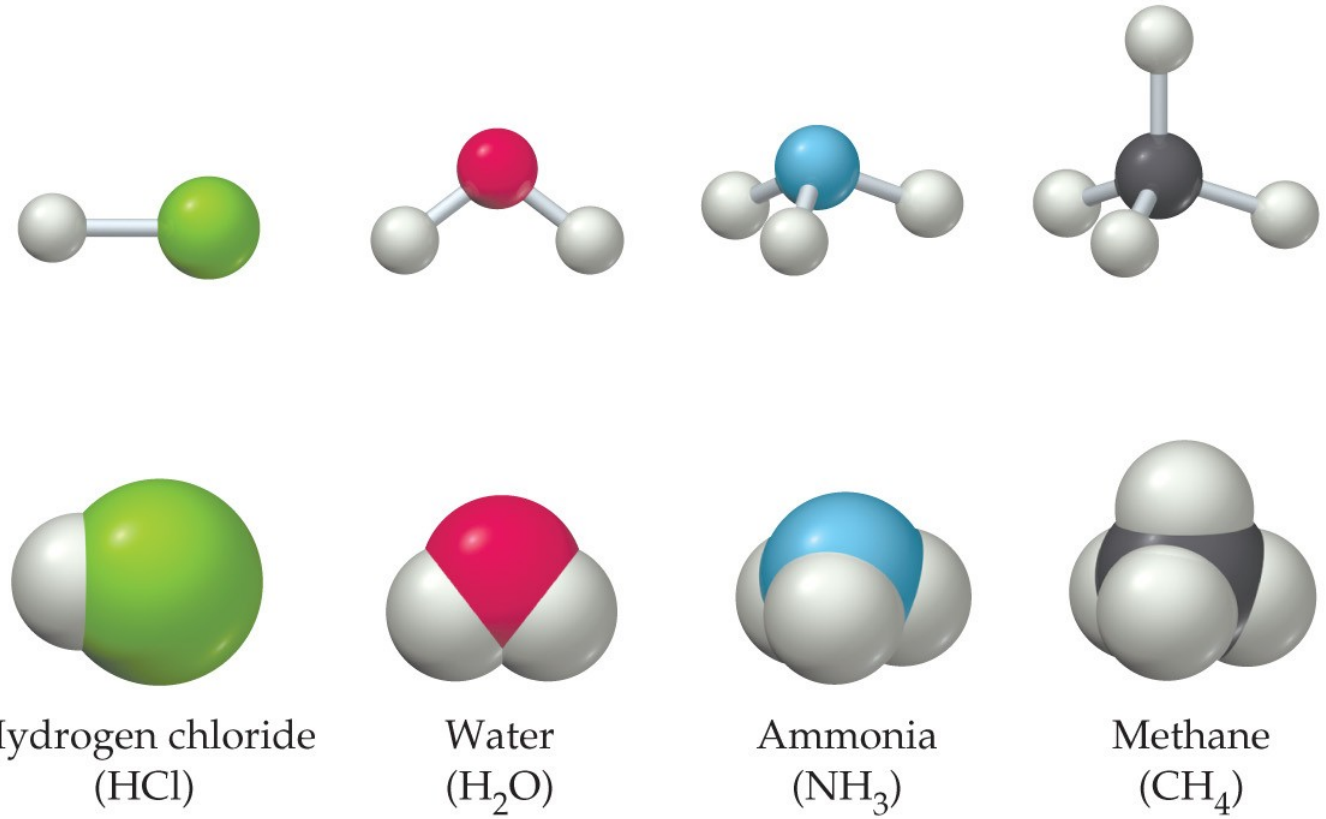


Similarly, two atoms are joined together when both nuclei (+) tug on the same electrons (dots).

Molecules, Ions, and Chemical Bonds – Models

Ball-and-stick models show atoms (spheres) joined together by covalent bonds (sticks).

Space-filling models portray the overall molecular shape but don't explicitly show covalent bonds.



Hydrogen chloride (HCl) | Water (H_2O) | Ammonia (NH_3) | Methane (CH_4)

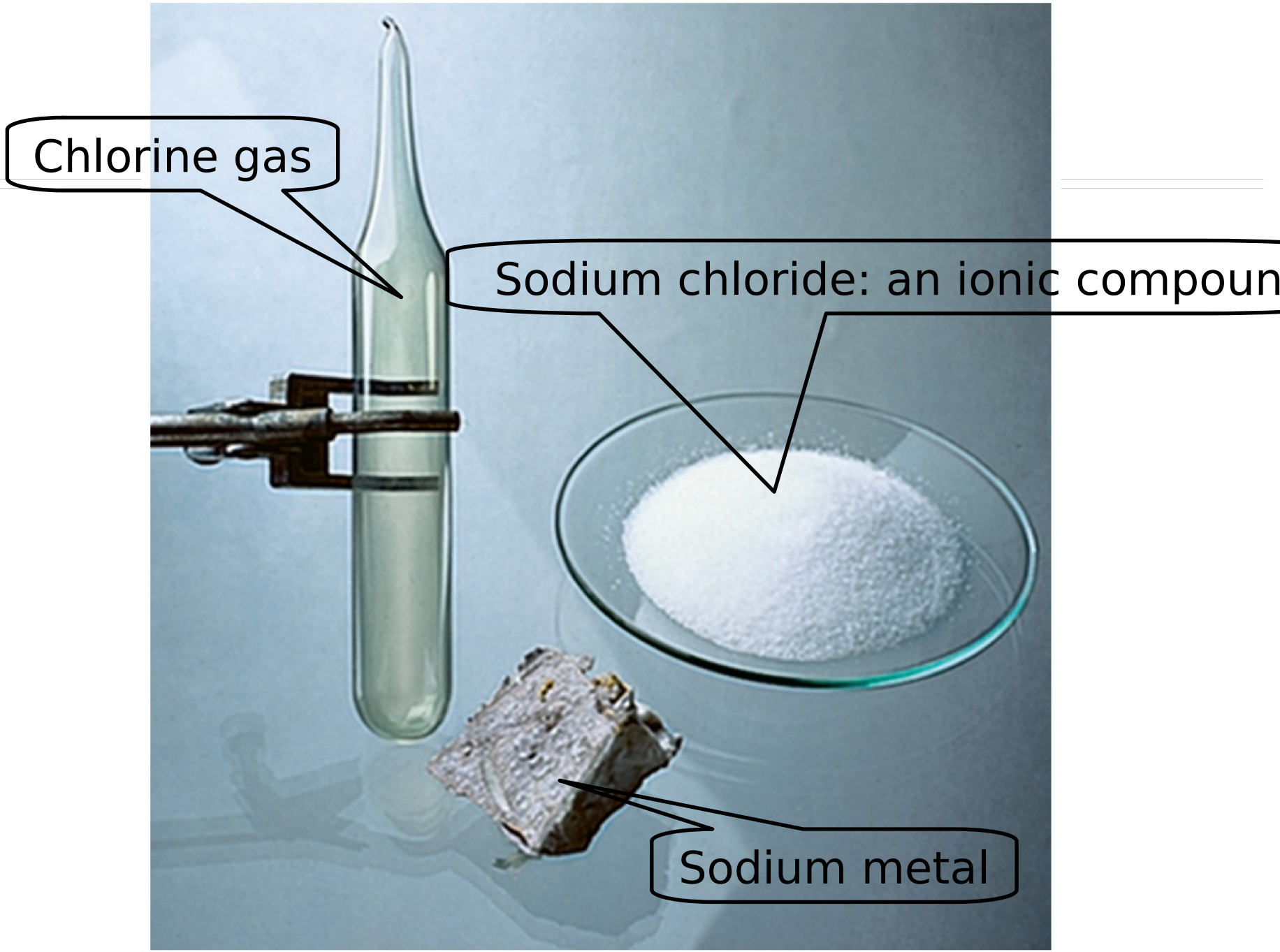
Molecules, Ions, and Chemical Bonds

Ion: A charged particle.

Cation: A positively charged particle. Metals tend to form cations.

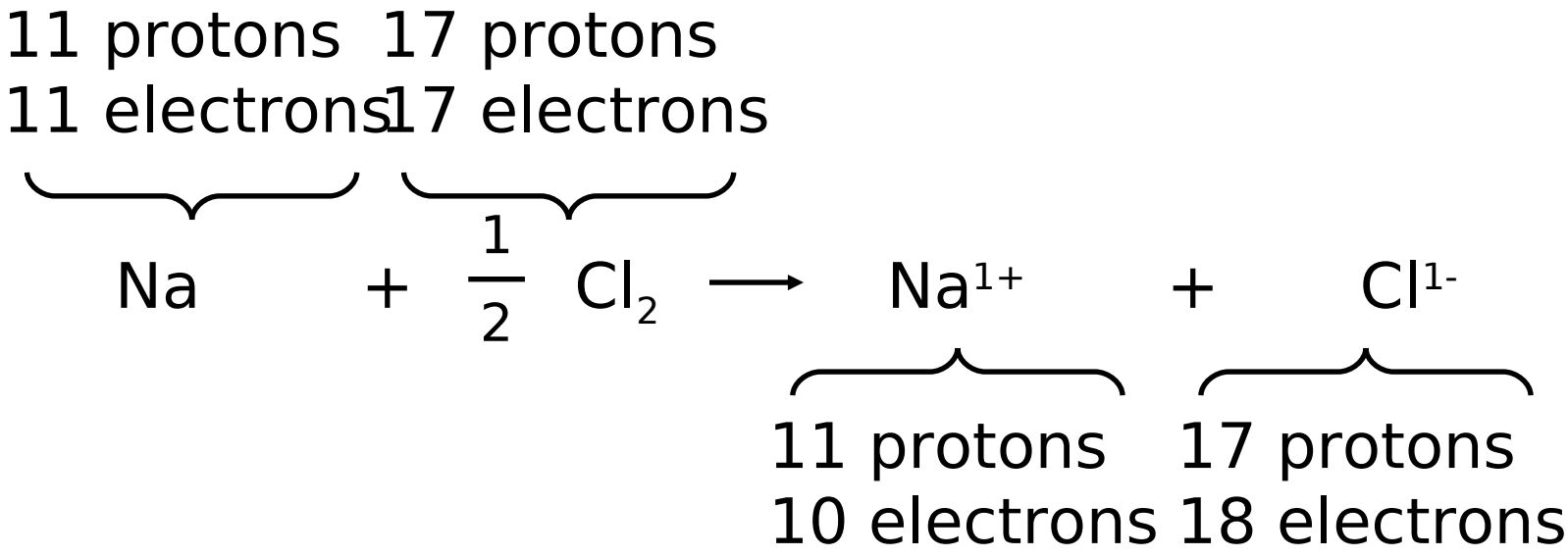
Anion: A negatively charged particle. Nonmetals tend to form anions.

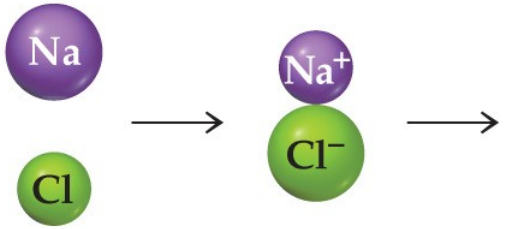
Ionic Bond: A transfer of one or more electrons from one atom to another. An electrostatic attraction between charged particles. Typically a metal bonded to a nonmetal.

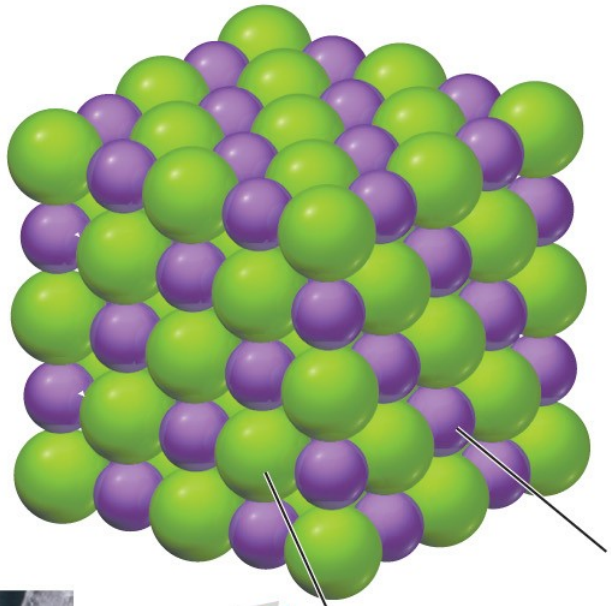

Chlorine gas
Sodium chloride: an ionic compoun
Sodium metal

Molecules, Ions, and Chemical Bonds

In the formation of sodium chloride, one electron is transferred from the sodium atom to a chlorine atom.







In the sodium chloride crystal, each **Na^+ ion** is surrounded by six nearest-neighbor **Cl^- ions** …

… and each **Cl^- ion** is surrounded by six nearest-neighbor **Na^+ ions**.

Electron Configurations of Ions

Atoms		Ions
Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$	$-e^-$ →	**Na^{1+}:** $1s^2\ 2s^2\ 2p^6$
Cl: $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^5$	$+e^-$ →	**Cl^{1-}:** $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^6$

Electron Configurations of Ions

TABLE 4.1 Some Common Main-Group Ions and Their Noble Gas Electron Configurations

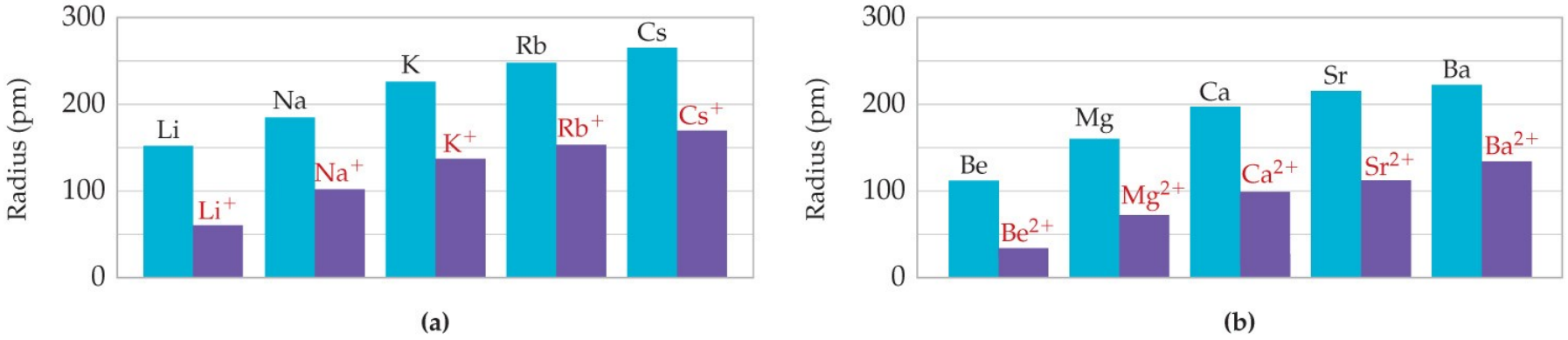
Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^+					[None]
H^-					[He]
Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}	$*Ga^{3+}$	S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}	$*In^{3+}$	Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}	$*Tl^{3+}$	Te^{2-}	I^-	[Xe]

*These ions don't have a true noble gas electron configuration because they have an additional filled *d* subshell.

Electron Configurations of Ions

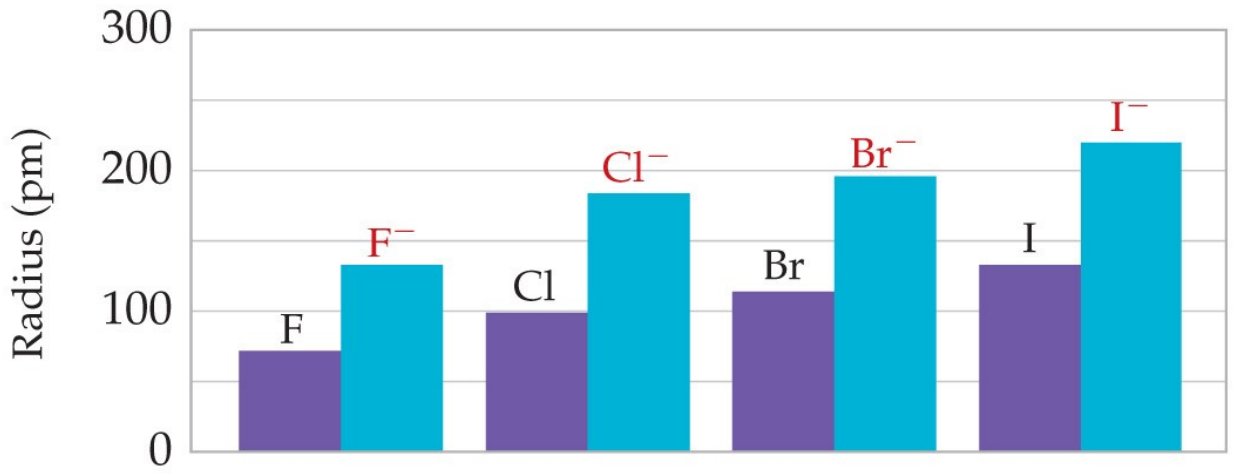
Atoms		Ions
Fe: [Ar] $4s^2$ $3d^6$	-2 e^- →	**Fe^{2+}:** [Ar] $3d^6$
Fe: [Ar] $4s^2$ $3d^6$	-3 e^- →	**Fe^{3+}:** [Ar] $3d^5$

Ionic Radii



Cations are smaller than their neutral atoms, both because the principal quantum number of the valence-shell electrons is smaller for the cations and because Z_{eff} is larger.

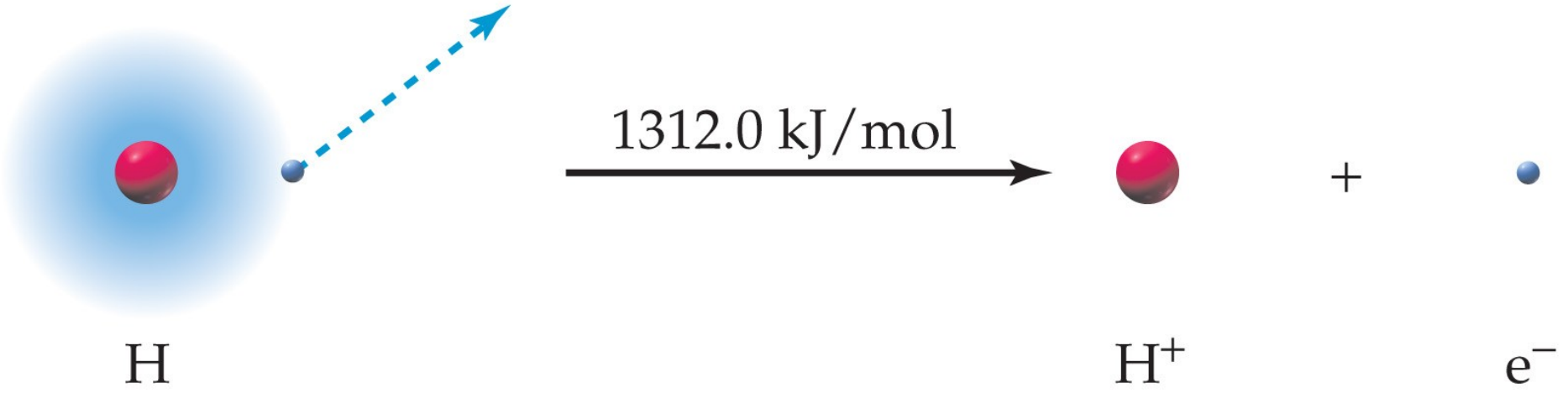
Ionic Radii



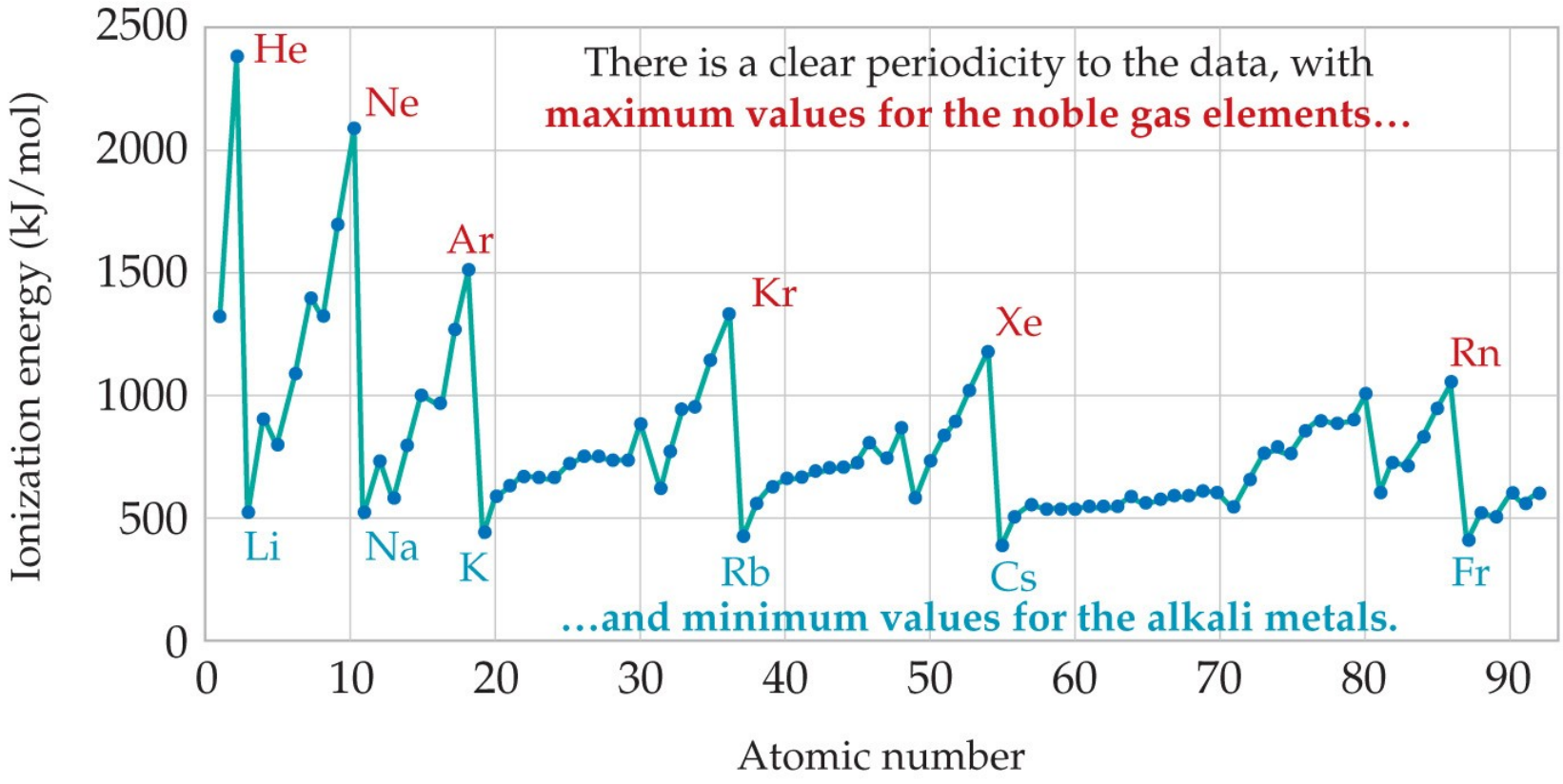
Anions are larger than their neutral atoms because of additional electron–electron repulsions and a decrease in Z_{eff}.

Ionization Energy

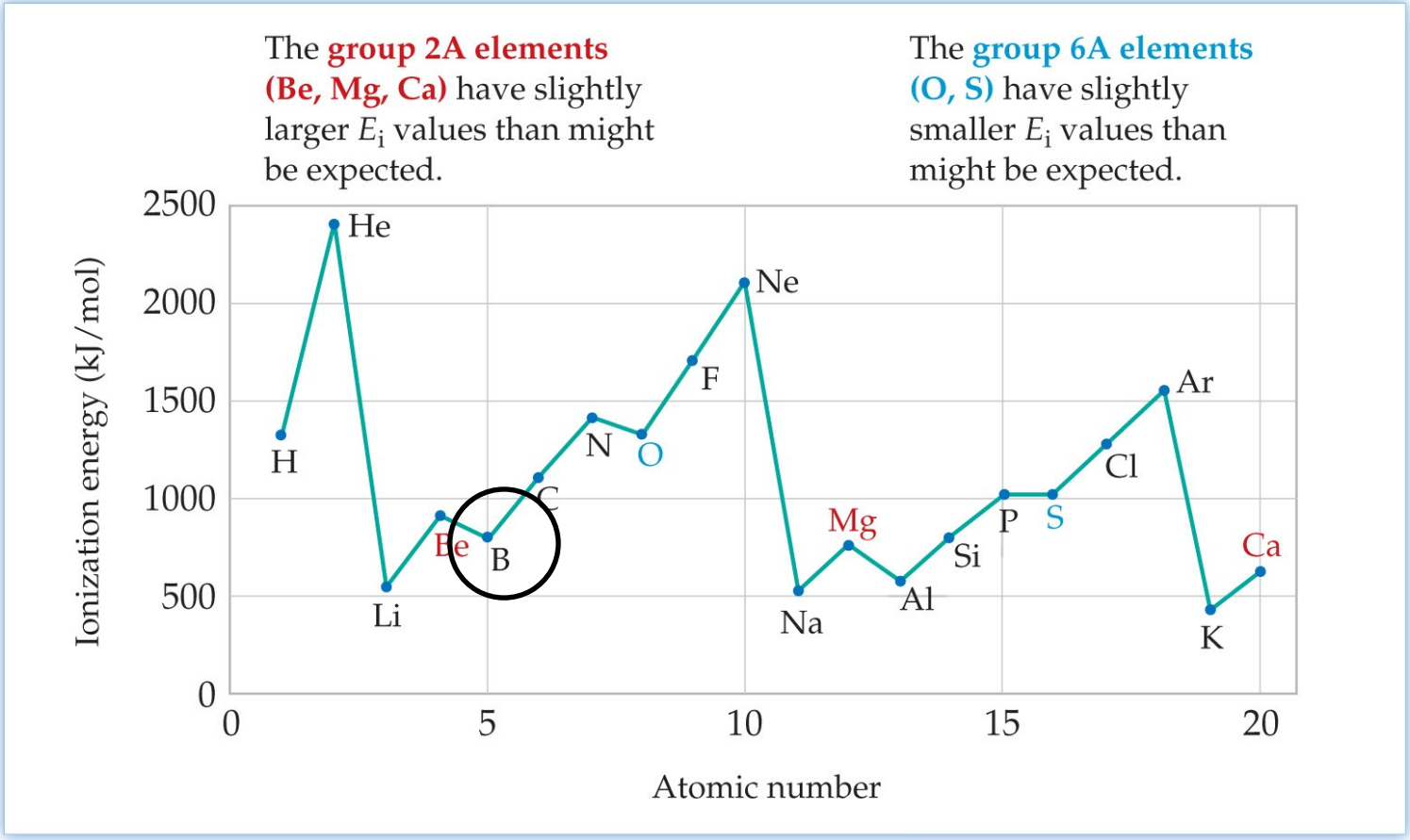
Ionization Energy (E_i): The amount of energy necessary to remove the highest-energy electron from an isolated neutral atom in the gaseous state



Ionization Energy

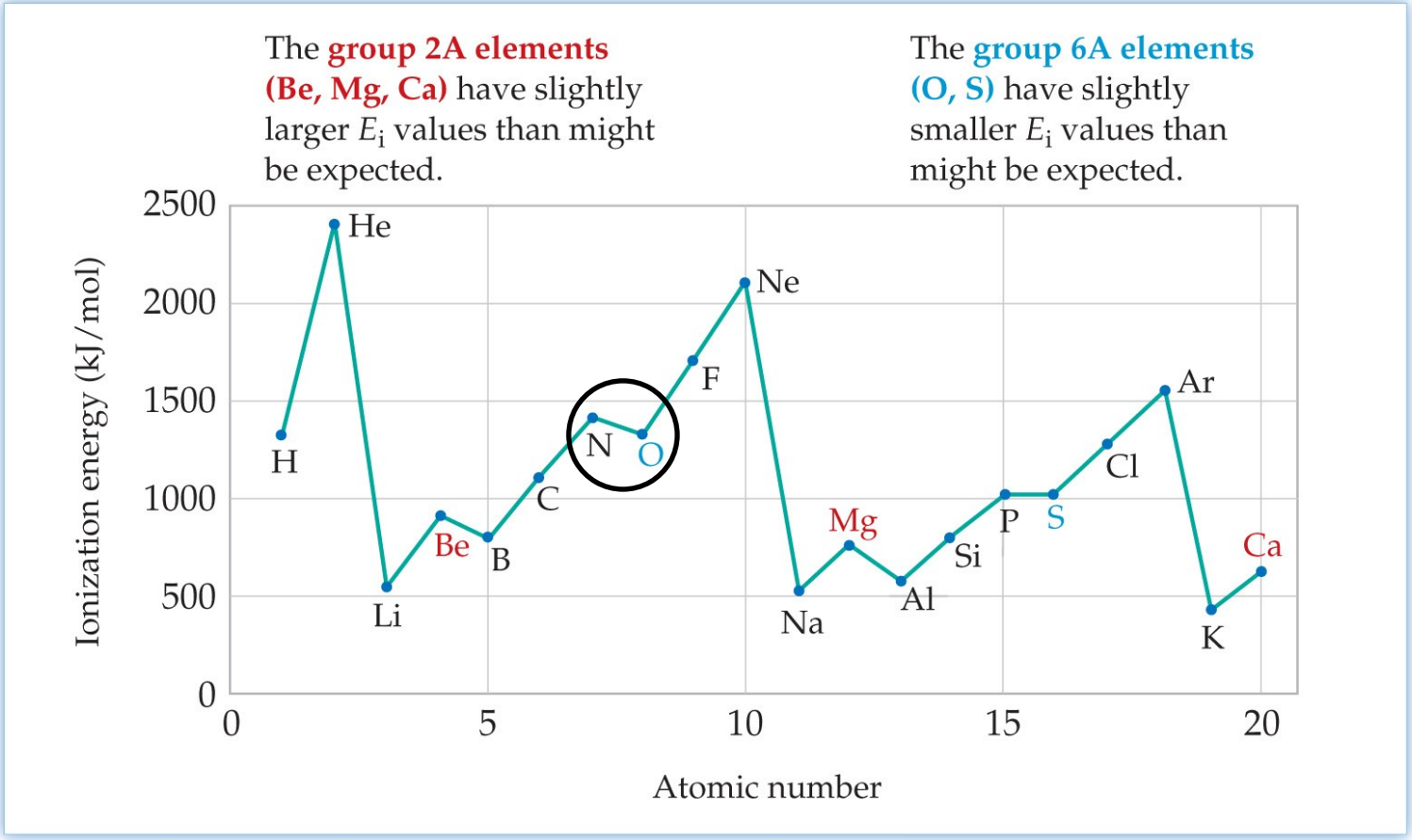


Ionization Energy



Boron has a lower E_i due to a smaller Z_{eff} (shielding by the $2s$ electrons)

Ionization Energy



Oxygen has a lower E_i since the first electron is removed from a filled

Rationale for higher E_i Values

- Be ($1s^2 2s^2$) Ei = 899.4 kJ/mol
- B ($1s^2 2s^2 2p^1$) Ei = 800.6 kJ/mol
- N ($1s^2 2s^2 2p^3$) Ei = 1402.3 kJ/mol
- O ($1s^2 2s^2 2p^4$) Ei = 1313.9 kJ/mol

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Higher Ionization Energy

$$M + \text{energy} \longrightarrow M^{1+} + e^-$$

$$M^{1+} + \text{energy} \longrightarrow M^{2+} + e^-$$

$$M^{2+} + \text{energy} \longrightarrow M^{3+} + e^-$$

TABLE 4.2 Higher Ionization Energies (kJ/mol) for Third-Row Elements

E_i Number	Na	Mg	Al	Si	P	S	Cl	Ar
E_{i1}	496	738	578	787	1,012	1,000	1,251	1,520
E_{i2}	4,562	1,451	1,817	1,577	1,903	2,251	2,297	2,665
E_{i3}	6,912	7,733	2,745	3,231	2,912	3,361	3,822	3,931
E_{i4}	9,543	10,540	11,575	4,356	4,956	4,564	5,158	5,770
E_{i5}	13,353	13,630	14,830	16,091	6,273	7,013	6,540	7,238
E_{i6}	16,610	17,995	18,376	19,784	22,233	8,495	9,458	8,781
E_{i7}	20,114	21,703	23,293	23,783	25,397	27,106	11,020	11,995

Why ?

$Na = (1s^2 2s^2 2p^6 3s^1) \rightarrow [Ne] \rightarrow (1s^2 2s^2 2p^5)$

E1 moves to [Ne] config.

E2 moves away from [Ne] config.

$Mg = (1s^2 2s^2 2p^6 3s^2) \rightarrow (1s^2 2s^2 2p^6 3s^1) \rightarrow [Ne]$

E1 moves to ½ filled s orbital config.

E2 moves to [Ne] config.

$Al = (1s^2 2s^2 2p^6 3s^2 3p^1) \rightarrow [Ne] \rightarrow (1s^2 2s^2 2p^6 3s^1)$

E1 moves to filled s orbital config.

E2 moves to ½ filled s orbital

E3 moves to [Ne] config.

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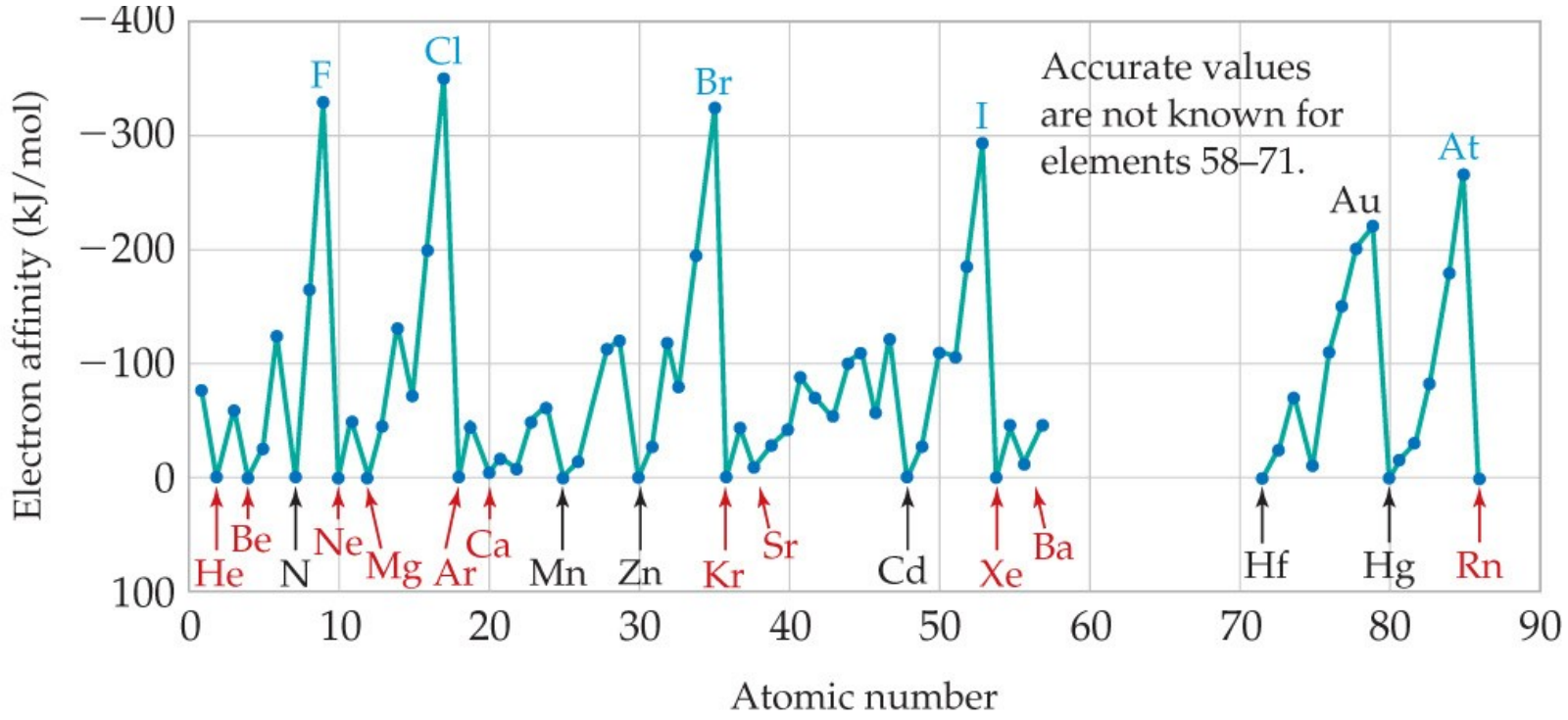
Electron Affinity

Electron Affinity (E_{ea}): The energy released when a neutral atom gains an electron to form an anion.

A negative value for E_{ea}, such as those for the **group 7A elements (halogens),** means that energy is released when an electron adds to an atom.

A value of zero, such as those for the **group 2A elements (alkaline earths) and group 8A elements (noble gases),** means that energy is absorbed but the exact amount can't be measured.



The Octet Rule

Octet Rule: Main-group elements tend to undergo reactions that leave them with *eight* outer-shell electrons.

TABLE 4.1 Some Common Main-Group Ions and Their Noble Gas Electron Configurations

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^+					[None]
H^-					[He]
Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}	$*Ga^{3+}$	S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}	$*In^{3+}$	Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}	$*Tl^{3+}$	Te^{2-}	I^-	[Xe]

*These ions don't have a true noble gas electron configuration because they have an additional filled *d* subshell.

The Octet Rule

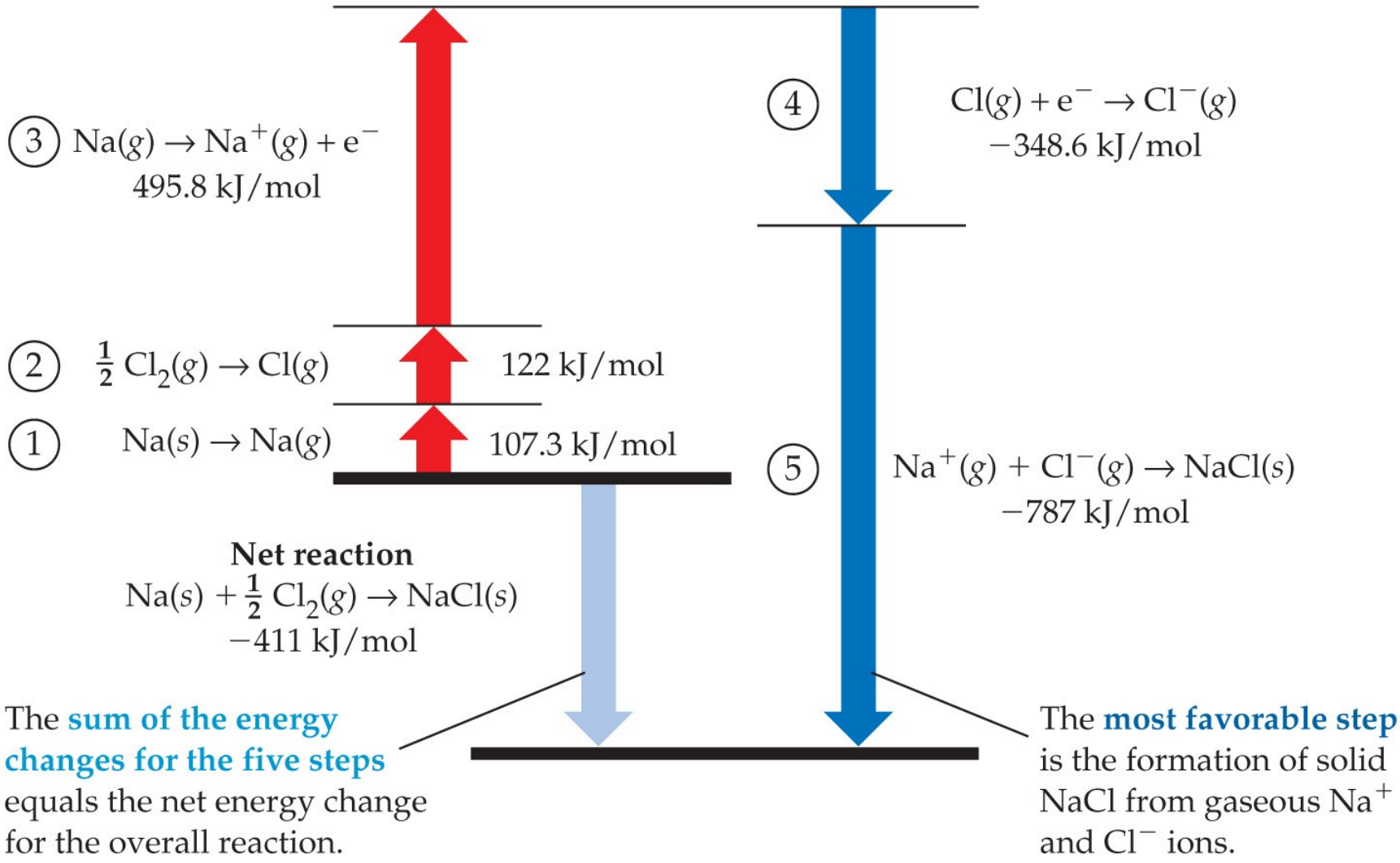
Octet Rule: Main-group elements tend to undergo reactions that leave them with *eight* outer-shell electrons.

Metals tend to have **low** E_i and **low** E_{ea}.

They tend to *lose* one or more electrons.

Nonmetals tend to have **high** E_i and **high** E_{ea}.

They tend to *gain* one or more electrons.


3 Na(g) → Na+(g) + e−
495.8 kJ/mol
4
Cl(g) + e− → Cl−(g)
−348.6 kJ/mol
2 ½ Cl2(g) → Cl(g)
122 kJ/mol
1 Na(s) → Na(g)
107.3 kJ/mol
5
Na+(g) + Cl−(g) → NaCl(s)
−787 kJ/mol
Net reaction
Na(s) + ½ Cl2(g) → NaCl(s)
−411 kJ/mol
The sum of the energy changes for the five steps equals the net energy change for the overall reaction.
The most favorable step is the formation of solid NaCl from gaseous Na+ and Cl− ions.

Ionic Bonds and the Formation of Ionic Solids

Born-Haber Cycle

Step 1: $Na(s) \rightarrow Na(g)$ +107.3 kJ/mol

Step 2: $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ +122 kJ/mol

Step 3: $Na(g) \rightarrow Na^{1+}(g) + e^-$ +495.8 kJ/mol

Step 4: $Cl(g) + e^- \rightarrow Cl^{1-}(g)$ -348.6 kJ/mol

Step 5: $Na^{1+}(g) + Cl^{1-}(g) \rightarrow NaCl(s)$ -787 kJ/mol

$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$ -411 kJ/mol

Lattice Energies in Ionic Solids

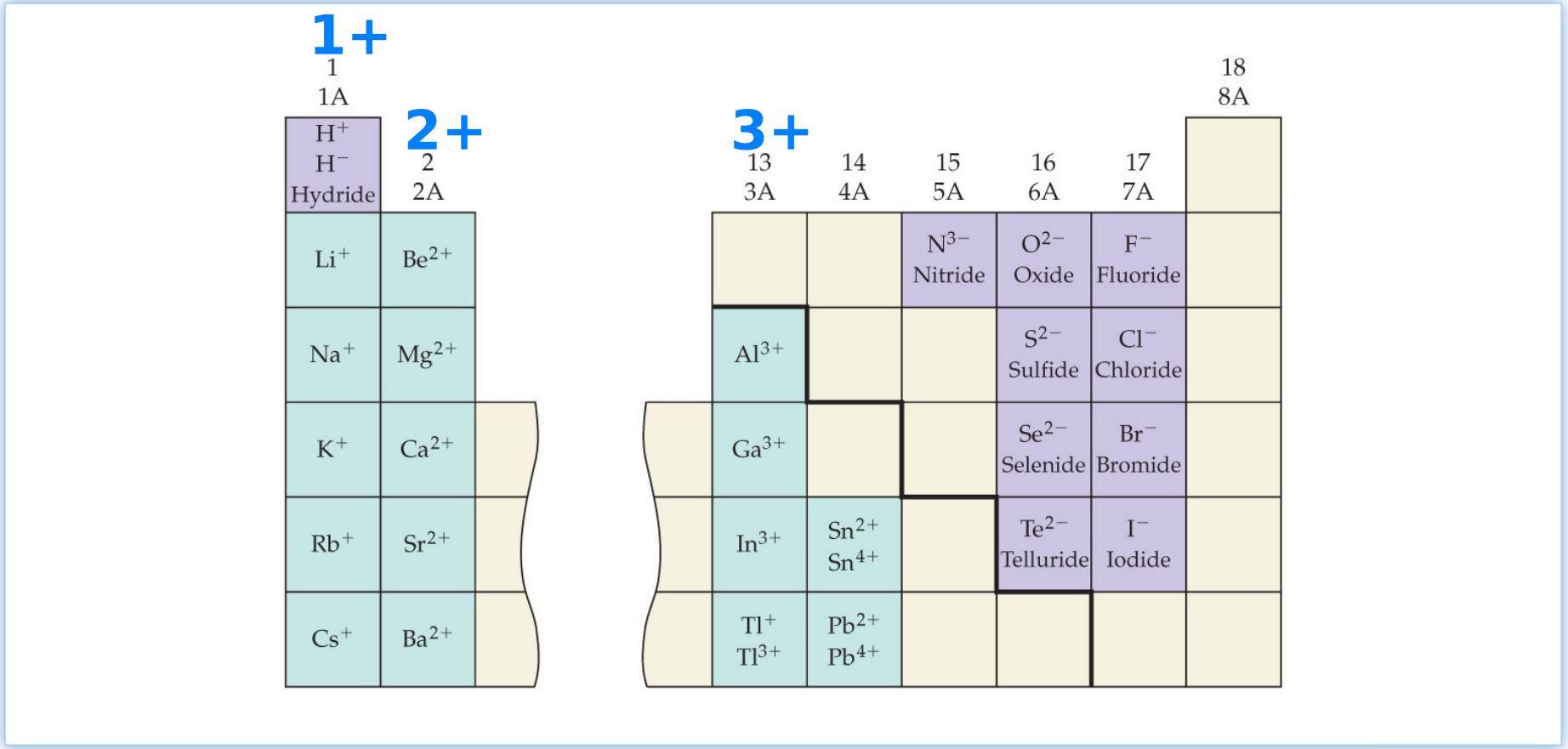
Lattice Energy *(U)*: The amount of energy that must be supplied to break up an ionic solid into individual gaseous ions.

TABLE 4.3 Lattice Energies of Some Ionic Solids (kJ/mol)

	Anion				
Cation	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1036	853	807	757	2925
Na^+	923	787	747	704	2695
K^+	821	715	682	649	2360
Be^{2+}	3505	3020	2914	2800	4443
Mg^{2+}	2957	2524	2440	2327	3791
Ca^{2+}	2630	2258	2176	2074	3401
Al^{3+}	5215	5492	5361	5218	15,916

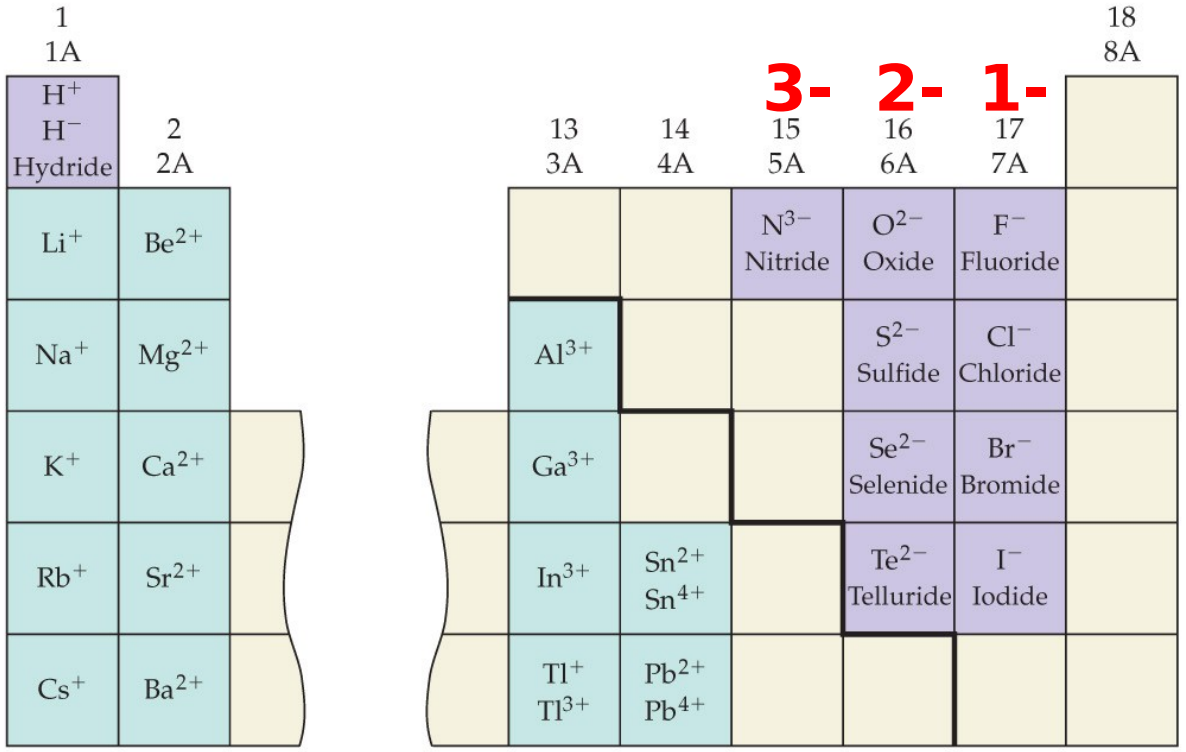
Naming Ionic Compounds

Cation Charges for Typical Main-Group Ions



Naming Ionic Compounds

Anion Charges for Typical Main-Group Ions



Naming Ionic Compounds

Some transition metals form more than one cation

3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B
Sc^{3+}	Ti^{3+}	V^{3+}	Cr^{2+} Cr^{3+}	Mn^{2+}	Fe^{2+} Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{+} Cu^{2+}	Zn^{2+}
Y^{3+}					Ru^{3+}	Rh^{3+}	Pd^{2+}	Ag^{+}	Cd^{2+}
									Hg^{2+}

Naming Ionic Compounds

Ionic Compound: A neutral compound in which the total number of positive charges must equal the total number of negative charges.

Binary Ionic Compounds

sodium chloride:	Na^{1+}	Cl^{1-}	NaCl
magnesium oxide:	Mg^{2+}	O^{2-}	MgO
aluminum sulfide:	Al^{3+}	S^{2-}	Al_2S_3

Naming Ionic Compounds

Use Roman numerals in parentheses to indicate the charge on metals that form more than one kind of cation.

Binary Ionic Compounds

iron(III) oxide:	Fe^{3+}	O^{2-}	Fe_2O_3
tin(II) chloride:	Sn^{2+}	Cl^{1-}	$SnCl_2$
lead(II) fluoride:	Pb^{2+}	F^{1-}	PbF_2

TABLE 4.4 Some Common Polyatomic Ions

Formula	Name
Cation	
NH_4^+	Ammonium
Singly charged anions	
$CH_3CO_2^-$	Acetate
CN^-	Cyanide
ClO^-	Hypochlorite
ClO_2^-	Chlorite
ClO_3^-	Chlorate
ClO_4^-	Perchlorate
$H_2PO_4^-$	Dihydrogen phosphate
HCO_3^-	Hydrogen carbonate (or bicarbonate)
HSO_4^-	Hydrogen sulfate (or bisulfate)
OH^-	Hydroxide
MnO_4^-	Permanganate
Singly charged anions (continued)	
NO_2^-	Nitrite
NO_3^-	Nitrate
Doubly charged anions	
CO_3^{2-}	Carbonate
CrO_4^{2-}	Chromate
$Cr_2O_7^{2-}$	Dichromate
O_2^{2-}	Peroxide
HPO_4^{2-}	Hydrogen phosphate
SO_3^{2-}	Sulfite
SO_4^{2-}	Sulfate
$S_2O_3^{2-}$	Thiosulfate
Triply charged anion	
PO_4^{3-}	Phosphate

Naming Ionic Compounds

Polyatomic Ionic Compounds

sodium hydroxide:	Na^{1+}	OH^{1-}	$NaOH$
magnesium carbonate:	Mg^{2+}	CO_3^{2-}	$MgCO_3$
sodium carbonate:	Na^{1+}	CO_3^{2-}	Na_2CO_3
iron(II) hydroxide:	Fe^{2+}	OH^{1-}	$Fe(OH)_2$

Chemistry of the Group 1A Elements: Alkali

TABLE 4.5 Properties of Alkali Metals

Name	Melting Point (°C)	Boiling Point (°C)	Density (g/cm^3)	First Ionization Energy (kJ/mol)	Abundance on Earth (%)	Atomic Radius (pm)	Ionic (M^+) Radius (pm)
Lithium	180.5	1342	0.534	520.2	0.0020	152	68
Sodium	97.7	883	0.971	495.8	2.36	186	102
Potassium	63.3	759	0.862	418.8	2.09	227	138
Rubidium	39.3	688	1.532	403.0	0.009 0	248	152
Cesium	28.4	671	1.873	375.7	0.000 10	265	167
Francium	—	—	—	~400	Trace	—	—

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- Metallic
- Bright, silvery
- Malleable
- Relatively soft
- Good conductors of electricity
- Very reactive
- Occur only in salts

Chemistry of the Group 1A Elements: Alkali Metals

Reaction with Halogens

$$2M(s) + X_2 \longrightarrow 2MX(s)$$

M = Li, Na, K, Rb, or Cs

X = F, Cl, Br, or I

Chemistry of the Group 1A Elements: Alkali Metals

Reaction with Oxygen

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s) \quad \text{oxide}$$

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s) \quad \text{peroxide}$$

$$K(s) + O_2(g) \longrightarrow KO_2(s) \quad \text{superoxide}$$

Chemistry of the Group 1A Elements: Alkali Metals

Reaction with Water

$$2M(s) + 2H_2O(l) \longrightarrow 2M^{1+}(aq) + 2OH^{1-}(aq) + H_2(g)$$

M = Li, Na, K, Rb, or Cs

Chemistry of the Group 1A Elements: Alkali Metals

Reaction with Ammonia

$$2M(s) + 2NH_3(l) \rightarrow 2M^{1+}(soln) + 2NH_2^{1-}(soln) + H_2(g)$$

M = Li, Na, K, Rb, or Cs

Chemistry of the Group 2A Elements: Alkaline Earth Metals

TABLE 4.6 Properties of Alkaline Earth Metals

Name	Melting Point (°C)	Boiling Point (°C)	Density (g/cm^3)	First Ionization Energy (kJ/mol)	Abundance on Earth (%)	Atomic Radius (pm)	Ionic (M^{2+}) Radius (pm)
Beryllium	1287	2471	1.848	899.4	0.000 28	112	44
Magnesium	650	1090	1.738	737.7	2.33	160	66
Calcium	842	1484	1.55	589.8	4.15	197	99
Strontium	777	1382	2.54	549.5	0.038	215	112
Barium	727	1897	3.62	502.9	0.042	222	134
Radium	700	1140	~5.0	509.3	Trace	223	143

- Metallic
- Bright, silvery
- Occur only in salts

- Relatively soft (harder than 1a
- Not as reactive as 1a

Chemistry of the Group 2A Elements: Alkaline Earth Metals

Reaction with Halogens

$$M + X_2 \longrightarrow MX_2$$

M = Be, Mg, Ca, Sr, or Ba

X = F, Cl, Br, or I

Chemistry of the Group 2A Elements: Alkaline Earth Metals

Reaction with Oxygen

$2M + O_2 \longrightarrow 2MO$ M = Be, Mg, Ca, Sr, or Ba

Chemistry of the Group 2A Elements: Alkaline Earth Metals

Reaction with Water

$$M(s) + 2H_2O(l) \longrightarrow M^{2+}(aq) + 2OH^{1-}(aq) + H_2(g)$$

M = Mg, Ca, Sr, or Ba

Chemistry of the Group 7A Elements: Halogens

TABLE 4.7 Properties of Halogens

Name	Melting Point (°C)	Boiling Point (°C)	Density (g/cm^3)	Electron Affinity (kJ/mol)	Abundance on Earth (%)	Atomic Radius (pm)	Ionic (X^-) Radius (pm)
Fluorine	−220	−188	1.50 (*l*)	−328	0.062	72	133
Chlorine	−101	−34	2.03 (*l*)	−349	0.013	99	181
Bromine	−7	59	3.12 (*l*)	−325	0.000 3	114	196
Iodine	114	184	4.930(*s*)	−295	0.000 05	133	220
Astatine	—	—	—	−270	Trace	—	—

- Nonmetals
- Exist as diatomics in elemental form
- Very reactive
- Occur only in salts and minerals

Chemistry of the Group 7A Elements: Halogens

Reaction with Metals

$$2M + nX_2 \longrightarrow 2MX_n$$

M = Metal

X = F, Cl, Br, or I

Chemistry of the Group 7A Elements: Halogens

Reaction with Hydrogen

$H_2(g) + X_2 \longrightarrow 2HX(g)$ X = F, Cl, Br, or I

Chemistry of the Group 8A Elements: Noble Gases

TABLE 4.8 Properties of Noble Gases

Name	Melting Point (°C)	Boiling Point (°C)	First Ionization Energy (kJ/mol)	Abundance in Dry Air (vol %)
Helium	−272.2	−268.9	2372.3	5.2×10^{-4}
Neon	−248.6	−246.1	2080.6	1.8×10^{-3}
Argon	−189.3	−185.9	1520.4	0.93
Krypton	−157.4	−153.2	1350.7	1.1×10^{-4}
Xenon	−111.8	−108.0	1170.4	9×10^{-6}
Radon	−71	−61.7	1037	Trace

- Colorless and odorless
- Nonmetals
- Very unreactive
- Occur naturally as atomic gases

Chemistry of the Group 8A Elements: Noble Gases

Reactions

$$Xe(g) + F_2(g) \longrightarrow XeF_2(s)$$

$$Xe(g) + 2F_2(g) \longrightarrow XeF_4(s)$$

$$Xe(g) + 3F_2(g) \longrightarrow XeF_6(s)$$